ENHANCED OIL RECOVERY FROM PYROLYSIS OF
VARIOUS AUSTRALIAN SHALES

Vetkav Parameswaran, Mark Polasky and Sunggyu Lee

Department of Chemical Engineering
The University of Akron.
Akron. Ohio 44325.

ABSTRACT

The oil yields from retorting Stuart, Rundle and Condor
shales have been optimized with respect to their process
operating conditions using a statistical experimental design
technique. A three factor, two level factorial design of
experiments was adopted to determine the main and interaction
effects of variables on the yield of oil from these shales. The
three variables are the particle size, the type of sweep gas and
the sweep gas flow rate.

It was found that retorting with carbon dioxide as the
sweep gas enhances the oil yield from Stuart shale by up to 24
percent. The strongest effect was observed from the sweep gas
flow rate and the optimal condition for this variable was found
through out-layer experiments. For each of the significant
effects, transport processes such as the combined heat and mass
transfer were explained and design criteria for a retorting
system were found for scale up purposes.

INTRODUCTION

Extensive deposits of oil shale, bearing enormous amounts
of equivalent synthetic fuel exist in the U.S.A., Australia,
Canada, China and various other parts of the world. However,
these deposits are far from uniform and there are wide variations
in the physical and chemical structure of the rocks even within
the same general location. As a result, engineering and
fundamental data are required even for preliminary design and
economic feasibility analysis. The need for data is even more
vital during the detailed industrial process development. In
order to maximize the yield, the kinetics as well as the physical
and chemical properties of the shale and shale oil must be
known. An extensive review of oil shale technology covering the
historical development and the kinetics of oil shale retorting as
well as the properties of oil shale has been presented by Branch
(1). This paper aims at finding the optimum operating conditions
for the retorting of Australian Tertiary shales. The shale
samples studied were taken from the Kerosene Creek member of the
Stuart deposit, the Ramsey crossing member of the Rundle deposit,
and the Brown oil shale unit of the Condor deposit, all of which
are located along the coastline of Queensland, Australia.

APPROACHES

Optimization studies generally involve either the solution of differential equations or the discrete techniques of linear algebra. In either case, it is necessary to have a mathematical description of the system. The physical and chemical complexity of oil shale renders such a rigorous mathematical treatment extremely difficult.

For engineering purposes however, an experimental exploration of the range of interesting process conditions can be coupled with the methods of statistical experimental design to arrive at optimum operating parameters with the minimum of experimental cost and effort. Therefore a three factor, two level design of experiments for each type of oil shale was adopted for this study.

IDENTIFYING THE CRITICAL VARIABLES

In order to ensure the reproducibility of experimental results, standard retorting procedures must be adopted without stifling the degree of freedom necessary to optimize the operating conditions. Twenty grams of oil shale were charged into the retort which was then heated at the rate of 10 C/min from 25 C to 700 C at atmospheric pressure. The details of the retorting apparatus have been published elsewhere (2). The apparatus consists essentially of a 15.75 inch long x 1 inch diameter stainless steel tube which is placed inside an electric furnace. The shale sample is loaded into the retort through a ball valve at the top of the tube. The sweep gas (which is preheated in a gas preheater following the reactor preheating schedule) flows down through the sample bed into an oil collection tube which is kept cool in a water bath.

The variables studied were the particle size (-8 +10 mesh and -20 +40 mesh (Tyler)), sweep gas type (carbon dioxide and nitrogen) and sweep gas flow rate (2 ml/sec and 5 ml/sec (STP)). The levels of these variables have been chosen based on preliminary experiments as well as prior experience (2).

The mechanism by which the oil is released from the pores of the shale is not very clear. The influence of the particle size on the retorter yield seems to depend on the type of oil shale being retorted. As the oil shales are fairly non-porous (very often below 5 % porosity), it is to be expected that crushing the oil shale would improve the process of oil evolution. However, there seems to be a minimum particle size below which the influence on the yield tends to be negative. This is due to the loss of kerogen entrapped in macropores while crushing. Therefore, two different sizes were tested, viz, -8 +10 mesh and -20 +40 mesh (Tyler).

It has been found by Lee (3), that carbon dioxide sweep gas conditions enhance the oil recovery from Colorado oil shales. Therefore tests were conducted with two types of sweep gas, i.e., nitrogen and carbon dioxide.

The flow rate of sweep gas is very important from an engineering point of view. This influences the heat and mass transfer conditions within the reactor and scale up and scale down of commercial reactors would be disastrous if the mass transfer conditions were not kept uniform in the scaled models. Therefore experiments were made with two different sweep gas flow rates, viz, 2 ml(STP)/sec and 5 ml(STP)/sec. This corresponds to vapor space velocities (calculated at STP) of 720 and 1800 per hour (superficial linear velocities of 0.4 and 1.0 cm/sec) respectively in the retort.

The influences of these three variables were studied on three different Australian Tertiary oil shales identified as Rundle, Stuart and Condor oil shales and the results were critically compared with those obtained with the Eastern and Western U.S. oil shales in terms of their yield, effects and optimal process conditions.

RESULTS AND DISCUSSION

The results of the various experiments conducted on Stuart, Rundle and Condor oil shales are presented in Table 1. The yields obtained were analyzed using Yates' algorithm (4) to determine the effects of the various treatment combinations on the yield. These effects are also summarized in Table 1. For the purpose of comparison, similar data are also included in Table 1 for the Colorado (5) and Ohio #2 (6) oil shales.

For the purpose of determining the significant effects, three replications were carried out and the effects that were larger than twice the standard deviation in these runs were identified as the significant effects. Accordingly, the minimum effects for the determination of significance were 4.80, 6.38, 2.34, 4.10, and 1.90 for the Stuart, Rundle, Condor, Colorado and Ohio # 2 shales respectively.

Stuart Shale

Of the three Australian shales tested, the Stuart shale gave the largest oil yield (Fischer Assay of 101 ml/kg) comparable to the yields obtained from most Colorado shales.

The sweep gas flow rate had the largest influence on the oil yield. This predominant effect was observed with all the oil shales so far tested. The influence in all cases was negative in the range of the variable studied indicating thereby that an increase in the flow rate from 2 ml(STP)/sec to 5 ml(STP)/sec reduces the yield. This strongly suggests that mass transfer

TABLE 1. Summary of Yields and Effects

Shale Type	Tertiary		Tertiary		Tertiary		Eocene		Devonian	
Treatment	STUART		RUNDLE		CONDOR		* COLORADO		* OHIO # 2	
Combination	Yield	Effect	Yield	Effect	Yield	Effect	Yield	Effect	Yield	Effect
(1)	105	110.94	80	63.13	65	51.72	94.2	92.94	32	25.75
a	125	- 4.38	82.5	1.25	67.5	- 0.31	95.8	0.57	31	2.50
b	130	5.63	65	- 5.00	60	- 2.81	105.9	8.72	29	2.00
ab	120	8.13	72.5	0	61.3	- 1.56	98.0	- 1.37	30	2.00
c	107.5	-18.13	50	-23.75	40	-23.44	81.0	-11.07	17	9.50
ac	95	9.38	50	- 3.75	40	2.19	83.3	3.72	19	-
bc	110	- 4.38	55	7.50	42.5	2.81	89.5	1.77	20	4.00
abc	95	6.88	50	- 2.50	37.5	- 0.94	95.8	3.37	28	1.00

Units of Yield are ml/kg
The significant effects are underlined

The Factors and the Levels are as follows:

Factor	+ Level	- Level
(a) Particle size	-8 +10 mesh	-20 +40 mesh
	-4 + 8 mesh(*)	
(b) Sweep Gas Type	Carbon Dioxide	Nitrogen
(c) Sweep Gas Flow	5 cc/sec	2 cc/sec
Heating Rate	---------- 10 C/min ----------	

Note:(*) Particle size of -4 + 8 mesh was used for the + Level
for the Colorado (5) and Ohio # 2 (6) shales.

plays an important role in shale oil extraction. Based on similar situations in gas-solid reaction systems, this implies that beyond a certain limit in the sweep gas flow rate, an increase in the flow rate adversely affects the total yield. Therefore, either a corner test or outlayer experiments have to be conducted to determine the optimal flow rate. In the corner test, the sweep gas flow rate was varied while keeping the other variables at their optimal values. The results show that the best yield is obtained with a sweep gas flow rate of 2 ml(STP)/sec.

On the other hand, the type of sweep gas used also has a significant effect on the yield. As the effect is positive, it can be concluded that carbon dioxide retorting enhances the yield. This was also the case with the Colorado and some Eastern U.S. Devonian shales (2,5). The role of carbon dioxide in enhancing the yield from such shales while having negative effects on the yield from other shales is not completely understood. However, the trend indicates that carbon dioxide enhances the retorting yield from shales with a large kerogen content. This influence is much less or even negative when the kerogen content is low (Fischer Assay below 30) or medium (Fischer Assay of the order of 60 to 70). It has been known among various investigators that kerogen swells better in a carbon dioxide medium than in a nitrogen medium. This should normally result in an improved yield; however, it also enhances the probability of caking or agglomeration inside and outside the shale particles. Therefore highly caking shales, such as the North Carolina lacustrine shale do not exhibit an increase in oil yield and this caking phenomenon is also observed.

The influence of the particle size on the oil yield was insignificant. However, the interaction effect of the gas flow rate and the particle size was negative and significant. This also shows that mass transfer plays an important role in the process. Even though improved mass transfer conditions around the shale particle should directly result in a smoother transport of oil and vapor products out of the sample bed, complex, semi-macroscopic phenomena such as the blockage of pore mouths, gel or liquid entrapment within the pores, formation of new pores, agglomeration of particles, etc., are not easily accounted for. Therefore, it can be said that the total yield of oil from oil shale is not only directly related to the heat and mass transfer conditions, but also to the morphological changes and the swelling of kerogen.

The largest yield was indeed obtained with small size particles and low sweep gas flow rates coupled with the use of carbon dioxide. The significance of carbon dioxide is also indicated by the large positive abc interaction effect.

It can therefore be concluded that the optimal operating conditions for retorting Stuart shale are:
1. Use carbon dioxide as the sweep gas.
2. Operate at low sweep gas flow rates,
   i.e., 2 ml(STP)/sec.
3. Use smaller particles, i.e., -20 +40 mesh.

Rundle Shale

The oil yield from Rundle shale was in the moderate range. The only significant main effect was from the sweep gas flow rate.

The influence of sweep gas flow rate in depressing the oil yield was most pronounced with the Rundle shale. Hence a corner test was performed by varying only the sweep gas flow rate while holding the particle size, type of sweep gas and the heating rate constant. The results show (Figure 1) that the optimal sweep gas flow rate is between 1 and 2 ml(STP)/sec.

It is interesting to note that even though carbon dioxide depresses the oil yield to a relatively insignificant extent, the interaction effect of the sweep gas type and flow rate is positive. This result also supports the prior conclusion that the oil yield is influenced not only by the mass transfer conditions, but also by the process of kerogen swelling and other morphological changes that occur during pyrolysis. The large interaction effect is shown schematically in a three-dimensional plot in Figure 2.

The optimal retorting conditions for the Rundle shale are therefore:
1. Use a sweep gas flow rate of 1.5 ml(STP)/sec.
2. Use nitrogen as the sweep gas, and
3. Use the larger size particles, i.e., -8 +10 mesh.

Condor Shale

The Condor shale yielded the smallest amount of oil per kilogram of sample. It was observed in this case also that the sweep gas flow rate had a large negative influence on the oil yield. Moreover, the use of carbon dioxide also depresses the yield. The standard experimental error calculated by conducting replicate experiments was smaller in this case than in the other two cases. Such an influence was also observed in the case of Ohio shale. The accuracy of experimentation is improved with smaller yields. It should be noted here that in the case of Ohio shale, the quantity of sample used was larger in order to improve the resolution of the experiments (6).

As in the case of Rundle shale, the optimal retorting conditions are:
1. Use lower sweep gas flow rate, i.e., 2 ml(STP)/sec.
2. Use smaller size particles, i.e., -20 +40 mesh.
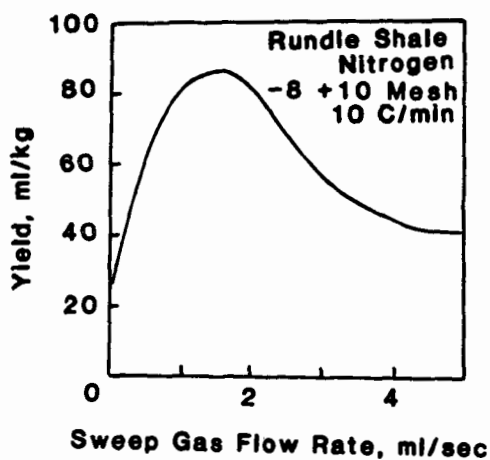3. Use nitrogen as the sweep gas.

Figure 1. Optimization of Sweep Gas Flow
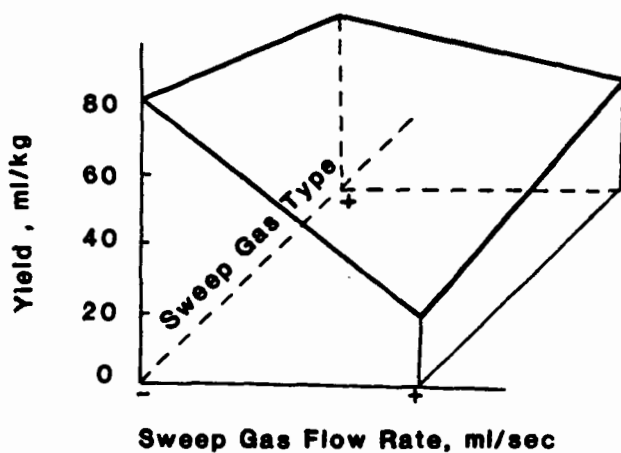Rate (ml (STP) of N_2 / Second).

Figure 2. Schematic Representation of the
Interactive Influence of Sweep Gas
Type and Flow Rate on the Yield
from Rundle Shale.

292

CONCLUSION

A statistical experimental approach was used to determine the optimal retorting conditions for three Australian oil shales. The optimal conditions are summarized below:

	Stuart	Rundle	Condor
Particle size:	-20 +40 mesh	-8 +10 mesh	-20 +40 mesh
Sweep Gas Type:	Carbon dioxide	Nitrogen	Nitrogen
Gas Flow Rate:	2 ml(STP)/sec	1.5 ml(STP)/sec	2 ml(STP)/sec

It is also concluded that the yield from oil shale pyrolysis is influenced by many mechanistic factors such as the heat and mass transfer conditions, the swelling of kerogen in the rock matrix, morphological changes during pyrolysis, agglomerating properties etc. Therefore, the factors investigated in this statistical optimization study represent a set of process variables that are most important for the successful design and operation of retorting equipment. The vapor hourly space velocity of the sweep gas was also calculated for scale up purposes.

REFERENCES

1. Branch M.C., Prog. Energy Combust. Sci., 5, pp 193 (1979).

2. Joshi R. and S. Lee, Liquid Fuels Technology, 1, pp 17 (1983).

3. Lee S., U.S. Patent No: 4,502,942. (1985).

4. Box G.E.P., W.G. Hunter, J.S. Hunter, Statistics for Experimenters, John Wiley and Sons, New York (1978).

5. Joshi R., Kinetic Study of Eastern Oil Shale Pyrolysis, Masters Thesis, The University of Akron (1983).

6. Lee S., M. Polasky, R. Joshi, Proceedings of 1983 Eastern Oil Shale Symposium, pp 225-233, University of Kentucky, Institute for Mining and Minerals Research (1984).